Carbon Fiber Adsorption Using Quantitative Structure-Activity Relationship

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ABSTRACT: Adsorption capacities of adsorbents are necessary for selecting and designing adsorption systems for separation and removal processes, such as air quality control devices, because they are indicators of service life. This paper describes the use of the Dubinin-Radushkevich (DR) equation and the quantitative structure-activated relationship to predict the equilibrium adsorption of select organic vapor by activated carbon fiber (ACF) adsorbents. The DR isotherm parameter, k, depends on the adsorbate as well as the adsorbent, and the prediction for k can be obtained indirectly from the affinity coefficient. A correlation is developed to compute the affinity coefficient from the modified, first-order, valence molecular connectivity index. This method provides an improved way to predict equilibrium adsorption capacities for select volatile organic compound adsorbates and activated carbon fiber adsorbents.

INTRODUCTION

Activated carbon fiber (ACF) in fabric or molded forms is an efficient microporous adsorbent for purifying indoor air and separating organic vapors in many industrial gas streams. Compared with conventional granular or powdered activated carbon, ACF has higher adsorption capacity, faster adsorption/desorption rates, and is suitable for in situ electrothermal regeneration (Petkovska, et al. 1991; Suzuki 1994; Rood et al. 1998; Sullivan et al. 1999). These advantages can lead to considerable reduction in the size of adsorption systems and the effort required to regenerate saturated adsorbent.

Selection and design of ACF adsorption systems requires knowledge of the adsorption capacities for the target organic vapors because they are often indicators of service life. Laboratory measurement of adsorption capacities may be hindered by chemical toxicity, equipment availability, analytical cost, and time requirements to complete the experiments. Therefore, it is advantageous to predict adsorption capacities using an adsorption isotherm model with parameters based on the physical properties of the adsorbent and the adsorbates.

The adsorption capacity for an organic vapor is related to its partial pressure at equilibrium by an adsorption isotherm. The Dubinin-Radushkevich (DR) equation is a commonly used pure component isotherm model that was developed from the Polanyi concept of adsorption potential and characteristic curves (Dubinin et al. 1991; Wood 1992; Dubinin 1985). The DR equation is written as

$$q = W_0\rho \exp\left[-k\left(RT \ln\left[\frac{P}{P_s}\right]\right)^2\right] \qquad (1)$$

and

$$k = \frac{k_s}{\beta^2} \qquad (2)$$

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where q = equilibrium adsorption capacity for the adsorbate; W_0 = limiting pore volume; ρ = density of condensed liquid in the micropores; k = DR isotherm parameter for the target adsorbate; R = universal gas constant; T = absolute temperature; P = partial pressure of the adsorbate; P_s = adsorbate's bulk saturation vapor pressure; k_s = DR isotherm parameter for the reference adsorbate; and β = affinity coefficient.

The isotherm parameters, W_0 and k, must be provided with (1) to calculate the adsorption capacity for an organic vapor. The limiting pore volume, W_0, is known as an adsorbent structure constant. The value of W_0 can be measured using one adsorbate, and that value can typically be applied to the same adsorbent that is adsorbing other similar adsorbates (Foster et al. 1992; Qi et al. 1998). Parameter k depends on the properties of the adsorbent and adsorbate. Experimental determination of k, or β if k_s is known, can be expensive and time consuming, and it is impractical to measure these values for all relevant adsorbate-adsorbent systems. These issues have caused interest in developing methods to predict k or β.

Conventionally, k is assumed to be the ratio of k_s and β^2 given by (2). Parameter k_s may be determined using a reference adsorbate such as benzene, for which $\beta \equiv 1.0$ (Dubinin 1975). The affinity coefficient has been correlated to the molecular parachor, the molar liquid volume, and the molar polarizability of adsorbates (Dubinin 1975; Wood 1992). Most recently, investigators (Nirmalakhandan and Speece 1993; Prakash et al. 1994) proposed the quantitative structure-activity relationship (QSAR) method to predict k directly without using a reference adsorbate. However, there is a lack of convincing evidence that demonstrates which of the physical parameters mentioned above correlate best with β and/or k.

The objective of this paper is to investigate two QSAR techniques for estimating the DR isotherm parameter k for adsorption of organic vapors by ACF adsorbents. A correlation is developed relating β to the molecular connectivity index. With this correlation, k may be calculated indirectly using (2). Results from the indirect QSAR method and the existing direct QSAR method (Nirmalakhandan and Speece 1993; Prakash et al. 1994) are then compared using experimental data for adsorption of benzene, acetone, and methyl ethyl ketone (MEK) onto three different microporous ACF adsorbents.

QSAR METHODS

The modified, first-order, valence molecular connectivity index, $^1\chi^v$, is a molecular structure descriptor originally developed by Kier and Hall (1986). As shown by Prakash et al. (1994), $^1\chi^v$ can be calculated directly from the molecular structure of a chemical by an algorithm requiring no experimental inputs. For this reason, $^1\chi^v$ was correlated to parameters k and β.

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In the direct QSAR method, k is assumed to be dependent on the adsorbate alone and practically independent of the adsorbent. By linear regression of the best-fit k values versus $^1\chi^v$ values, Nirmalakhandan and Speece (1993) developed the following correlation:

$$\log k = 1.585 - 0.442\,^1\chi^v, \quad (r^2 = 0.924) \qquad (3)$$

The units of k in (3) are 10^{-8} mol^2/cal^2.

The best-fit k value was determined by minimizing the difference between equilibrium adsorption capacities predicted by the DR equation and the experimental adsorption isotherm values for select combinations of organic vapors and granular and powdered activated carbon adsorbents. As pointed out by Prakash et al. (1994), the advantage of this approach is that no reference chemical and experimental inputs are required to estimate k. However, to use the DR Equation, W_0 must be known. The value for W_0 may be determined from isotherm data using a representative adsorbate such as benzene or water vapors (Foster et al. 1992; Qi et al. 1998).

The indirect QSAR method uses the conventional approach that considers interactions between the adsorbate and adsorbent described by (2) with the independent parameters, k_s and β. The following correlation relates β to $^1\chi^v$:

$$\beta = 0.3690\,^1\chi^v + 0.2729, \quad (r^2 = 0.967) \qquad (4)$$

Eq. (4) was developed by linear regression of the best-fit k values versus $^1\chi^v$ values, where the best-fit k values were determined using the experimental data of Cal (1995) for adsorption of benzene, acetone, and MEK onto three ACF adsorbents. The adsorbents were manufactured from cross-linked phenol-aldehyde fibers by American Kynol, Inc. (Table 1). The limiting pore volume, W_0, was determined simultaneously with k_s using benzene as a reference chemical.

ANALYSIS OF QSAR METHODS

The two QSAR methods were evaluated using the experimental data of Cal (1995) for adsorption of benzene, acetone, and MEK onto three different ACF adsorbents (Table 1). The adsorption experiments were performed using a gravimetric balance (Cahn Model 2000) at room temperature ($\sim$25°C) and a total pressure of 1 atm (Cal 1995). There are nine adsorption isotherms that were generated with more than 100 data points using organic vapor concentrations in the ppmv range. The saturated vapor pressures of the organic compounds were estimated using the Wagner equation (Reid et al. 1986), and the density of the organic compound as a bulk liquid was determined by Beaton and Hewit (1989). For each adsorbent, W_0 and k_s (with $\beta = 1.0$) were determined by minimizing the difference between the results from the DR equation and the benzene adsorption isotherm data.

Values for k estimated with the direct QSAR method (3) are compared with the corresponding k values estimated with the best-fit k values in Table 2. For adsorption of benzene, acetone, and MEK onto ACF-20 and ACF-25, the estimates by the direct QSAR and the best-fit k methods agree within a maximum difference of 16%. However, the differences in estimated k values are much higher for the three organic vapors that adsorbed onto ACF-15 (63–96% difference). This may result from not considering the adsorbate-adsorbent interactions. Consequently, the DR equation with k calculated by the direct QSAR method significantly underestimates the adsorption isotherms for the organic vapor-ACF-15 systems (Fig. 1). The average errors are 27, 35, and 62% for benzene, MEK, and acetone, respectively, when using the direct QSAR method to estimate k.

Table 2 also compares k values estimated with the indirect QSAR method and the best-fit k values. The k values estimated indirectly using (2) and (4) appear to agree well with the best-fit k values for the three adsorbates onto the three ACF adsorbents (11, 5, and 2% maximum differences for ACF-15, ACF-20, and ACF-25, respectively). This may be attributed to the consideration of both adsorbent and adsorbate by the indirect QSAR method. With the estimated k values and the DR equation, the adsorption isotherms are computed and compared with the measured isotherm data in Figs. 2–4. The DR equation agrees well with the measured isotherm data for adsorption of benzene and acetone onto the three ACF adsorbents. Similar results are shown for MEK on ACF-15 and ACF-20. However, the DR equation underestimates the ad-

TABLE 1. Properties of Activated Carbon Fiber Adsorbents

Property (1)	ACF-15 (2)	ACF-20 (3)	ACF-25 (4)
BET specific surface area (P/P_s for N_2) = 10 $-$ 5 to 0.4 at 77 K) (m^2/g)[a]	730	1,330	1,860
C/H/O/N (mass percent)[b]	92.8/1.04/6.12/<0.05	95.4/.68/3.92/<0.05	95.4/0.59/3.07/<0.05
Pore size with maximum volume (nm)[c]	7.0	—	9.0

[a]Cal 1995.
[b]Foster et al. 1992.
[c]Sun et al. 1998.

TABLE 2. Comparison of Computed and Best-Fit DR Isotherm k Values[a]

Adsorbent (1)	Chemical (2)	W_0 (cm^3/g) (3)	$^1\chi^v$ (4)	β (5)	Best-fit k $(mole/KJ)^2$ ($k \times 10^3$) (6)	Direct QSAR k $(mole/KJ)^2$ ($k \times 10^3$) (7)	Indirect QSAR k $(mole/KJ)^2$ (8)
ACF-15	Benzene	0.457	2.0	1.01	1.77[a]	2.87	1.73×10^{-3}
	Acetone	0.457	1.2	0.72	3.85	6.47	3.46×10^{-3}
	MEK	0.457	1.76	0.92	1.87	3.66	2.08×10^{-3}
ACF-20	Benzene	0.715	2.0	1.01	3.20	2.87	3.13×10^{-3}
	Acetone	0.715	1.2	0.72	5.96	6.47	6.24×10^{-3}
	MEK	0.715	1.76	0.92	3.70	3.66	3.74×10^{-3}
ACF-25	Benzene	0.563	2.0	1.01	3.42	2.87	3.35×10^{-3}
	Acetone	0.563	1.2	0.72	6.57	6.47	6.67×10^{-3}
	MEK	0.563	1.76	0.92	4.08	3.66	4.02×10^{-3}

[a]$k = 1.77 \times 10^{-3}$ $(mole/KJ)^2$.

sorption capacity for MEK on ACF-25 as the vapor concentration increases. The largest average error for any of the computed isotherms in Figs. 2–4 is 14%.

It is important to note that the original direct QSAR method was developed using a broad database while the indirect QSAR method presented here was developed using the limited ACF data of Cal (1995) to which it has also been compared. This may have contributed to the larger regression coefficients, r^2, of the indirect method compared with the direct method.

In this study, benzene was used as the reference chemical, although theoretically any chemical can be chosen. Benzene is nonpolar, while acetone and MEK are polar. The reasonable approximations of the adsorption data for these three organic vapors by the indirect QSAR method indicate that the chemical polarity has a limited effect on β.

Table 3 compares the values for β estimated using three different predictive methods for selected organic vapors. These methods are correlations relating β to the molecular connectivity index, the molecular parachor, and the molar polarizability, respectively. A detailed description of the molecular parachor method and the polarizability method are available in the literature (Dubinin 1975; Dubinin 1991; Cal 1995). As shown in Table 3, the three methods provide similar estimates for β. The estimated β values by the indirect QSAR method can be linearly correlated with those estimated by the other two methods with a regression coefficient of $r^2 = 0.97$. This
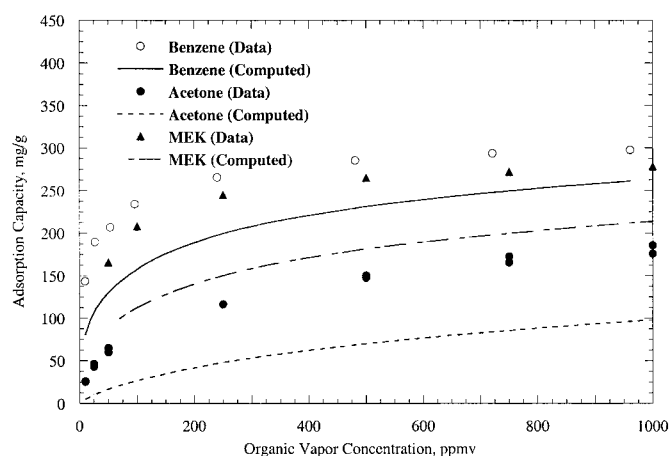

FIG. 1. Measured and Computed Adsorption Isotherms Using DR Equation with _k_ Values from Direct QSAR Method for Benzene, Acetone, and MEK on ACF-15 Systems
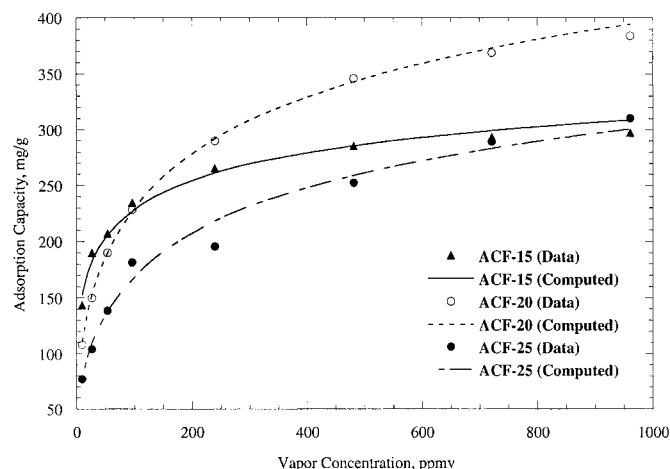

FIG. 2. Measured and Computed Adsorption Isotherms Using DR Equation with _k_ Values from Indirect QSAR Method for Benzene on 3 ACF Adsorbents
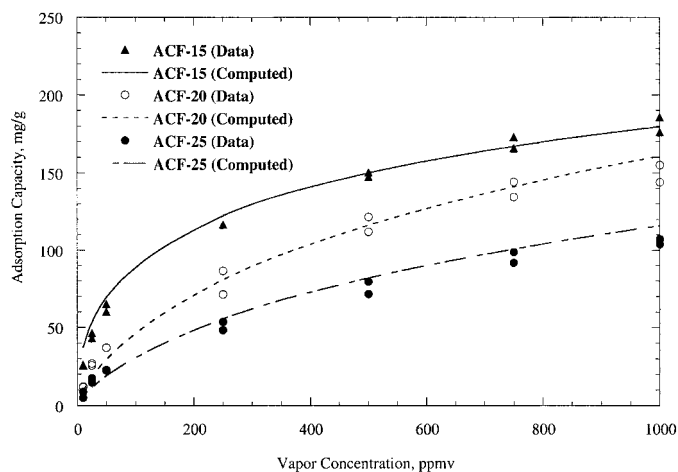

FIG. 3. Measured and Computed Adsorption Isotherms Using DR Equation with _k_ Values from Indirect QSAR Method for Acetone on 3 ACF Adsorbents
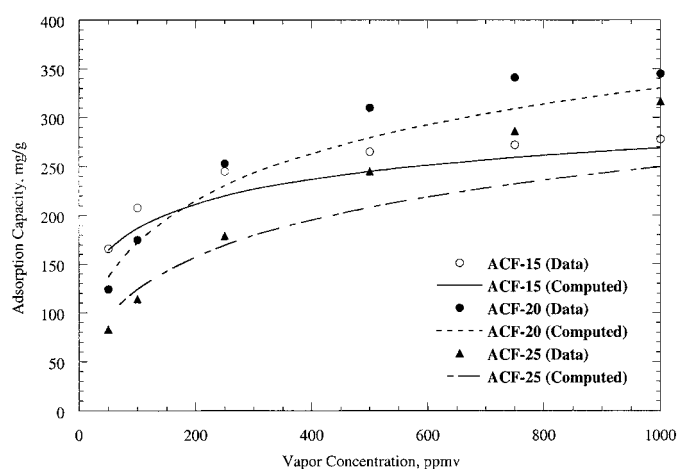

FIG. 4. Measured and Computed Adsorption Isotherms Using DR Equation with _k_ Values from Indirect QSAR Method for MEK on 3 ACF Adsorbents

TABLE 3. Values[a] for Affinity Coefficient Estimated Using Select Methods and Organic Vapors

Chemical (1)	Indirect QSAR β (2)	Parachor β (3)	Polarizability β (4)
Acetaldehyde	0.53	0.65	0.43
Acetone	0.72	0.78	0.61
Benzene	1.01	1.00	1.00
Ethyl Chloride	0.83	0.72	0.873
MEK	0.92	0.96	0.81
Tetrachloride	1.11	—	1.12
Toluene	1.16	1.19	1.20
P-xylene	1.31	1.38	1.38

[a]Based on benzene as reference chemical.

suggests that the indirect QSAR method should be useful beyond the limited database tested here.

SUMMARY AND CONCLUSIONS

This paper demonstrates the use of the Dubinin-Radushkevich (DR) equation and the quantitative structure-activated relationship (QSAR) methods to estimate the adsorption capacities of select organic vapors and activated carbon fiber (ACF) adsorbents. Two QSAR methods are evaluated using the experimental data for adsorption of benzene, acetone, and methyl

ethyl ketone onto three different ACF adsorbents. It is suggested that the DR isotherm parameter k depends on the adsorbate as well as the adsorbent, and an improved prediction for k may be obtained indirectly from the affinity coefficient. A correlation is presented to compute the affinity coefficient from the modified, first-order, valence molecular connectivity index.

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APPENDIX II. NOTATION

The following symbols are used in this paper:

k = DR isotherm parameter for target adsorbate (mole/kJ)^2;
k_s = DR isotherm parameter for reference adsorbate;
P = partial pressure of target adsorbate;
P_0 = saturation partial pressure of target adsorbate;
q = adsorption capacity (mg/g);
R = universal gas constant;
r^2 = regression coefficient;
T = absolute temperature (K);
W_0 = limiting pore volume (cm^3/g);
β = affinity coefficient;
ρ = density of condensed liquid in micropores (g/cm^3); and
$^1\chi^v$ = molecular connectivity index.